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STABLE ISOTOPIC COMPOSITIONS OF DIAGENETIC CARBONATE IN HEMIPELAGIC AND
TERRIGENOUS SUBMARINE FAN STRATA, BARBADOS, WEST INDIES

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ABSTRACT

Diagenetic carbonate nodules and cements occur in organic carbon-rich terrigenous and hemipelagic strata of the basal complex on Barbados Island in the crestal zone of the Barbados accretionary prism. The carbonate has no apparent association with deformational structures, and various lines of geologic evidence suggest that it is a product of early diagenesis. Isotopic compositions of such carbonate can be successfully interpreted using a standard model of organic burial diagenesis. Some of the diagenetic carbonate has positive $\delta^{18}\text{O}$ values and zoned or highly negative $\delta^{13}\text{C}$ values indicative of precipitation at relatively low temperatures and shallow depths (0-100 m) in the aerobic and sulfate reduction zones and (or) near the top of the carbonate reduction zone. Other carbonate has more negative $\delta^{18}\text{O}$ values and positive $\delta^{13}\text{C}$ values, suggestive of at relatively greater temperatures and depths (≥ 500 m) within the zone of carbonate reduction and (or) early thermal diagenesis. The early diagenesis probably occurred in early-late Eocene time, prior to offscrape and accretion of beds of the basal complex. Lack of systematic correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the diagenetic carbonate suggests spatial and (or) temporal variability in depth of organic burial diagenetic zones in the predeformed succession of marine strata.

INTRODUCTION

Carbonate nodules and cements of probable early diagenetic origin occur in organic carbon-rich terrigenous and hemipelagic strata that crop out on Barbados Island in the crestal zone of the Barbados accretionary prism (Fig. 1A). In this paper, we describe the petrography, mineralogy, and stable carbon and oxygen isotopic compositions of the early diagenetic carbonate and give interpretations of the significance of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions for the relative ages, temperatures, and depths of carbonate precipitation. A companion paper (Torrini et al., 1990) describes diagenetic carbonate of probable late origin that occurs exclusively in fault zones and mud diapirs of Barbados.

Thirty-five samples were collected from the freshly fractured faces of beds and nodules. For certain nodules, cores were sampled along with rims and cross-cutting veins. The mineralogy of individual samples was determined by powder X-ray diffraction (XRD), and separates of all powdered samples were analyzed at the U. S. Geological Survey, Lakewood, Colorado for carbon and oxygen isotopic composition. Calcite, dolomite, and siderite were identified based on their characteristic $d(104)$ spacings. Ferroan dolomite was identified based on its rhombohedral morphology in thin section and on the dominance of iron vs. calcium and magnesium on its EDX spectrum. Data for both oxygen and carbon isotopes are presented

in the normal δ notation with reference to PDB standard.

GEOLOGY OF BARBADOS

The island of Barbados exposes the structural high of the accretionary prism of the active Lesser Antilles forearc (Speed and Larue, 1982; Speed, Westbrook et al., 1984). The Scotland district of Barbados (Fig. 1B) is an erosional window through Pleistocene reef that caps the majority of the island. Outcrop and well studies indicate the existence of three major tectonic units beneath the reefcap (Fig. 1B) (Speed, 1988 and references therein). The highest unit is the Oceanic allochthon, which consists of interbedded pelagic and volcanogenic Cenozoic rocks that were thrust east above the prism's structural high from the adjacent forearc basin. The intermediate unit is sporadically occurring prism cover. The lowest unit is the basal complex, which is an assemblage of fault-bounded packets of siliciclastic turbidites and hemipelagic strata of probable early to late Eocene depositional age. The basal complex, which forms the foundation of the structural high of the accretionary prism and extends to depths ≥ 4 km, is thought to have formed by offscrape and accretion in late Eocene time. Diapirs of organic carbon-rich, mud-matrix melange cut the basal complex and locally the Oceanic nappes (Speed, 1988).

Rocks of the Basal Complex

There are no evident correlations among sequences of beds in different fault-bounded packets of the basal complex. Relative stratigraphic positions are known only on an intrapacket basis.

Terrigenous beds of the basal complex are about half quartz-rich turbiditic sandstone and half illite- and kaolinite-rich mudstone (Larue and Speed, 1985). Mudstones contain Type III kerogen and 0.3 - 4.0 wt% total organic carbon. With the exception of rare planktics (nannofossils) and coarse resedimented shallow-water fossils, the terrigenous strata are virtually noncalcareous. The terrigenous sediment, of continental provenance, was derived from cratonal South America and probably deposited in a trench wedge and (or) varied sites on one or more submarine fans (Larue and Speed, 1985; Kasper and Larue, 1986).

Hemipelagic rocks of the basal complex include radiolarite, radiolarian mudstone, and radiolarian-bearing muddy, quartzose turbidites of early and middle Eocene age. Such rocks are generally more smectite-rich than terrigenous strata of the basal complex, contain both Type II and Type III kerogen, and have total organic carbon values of 1.8-10.7 wt.%.

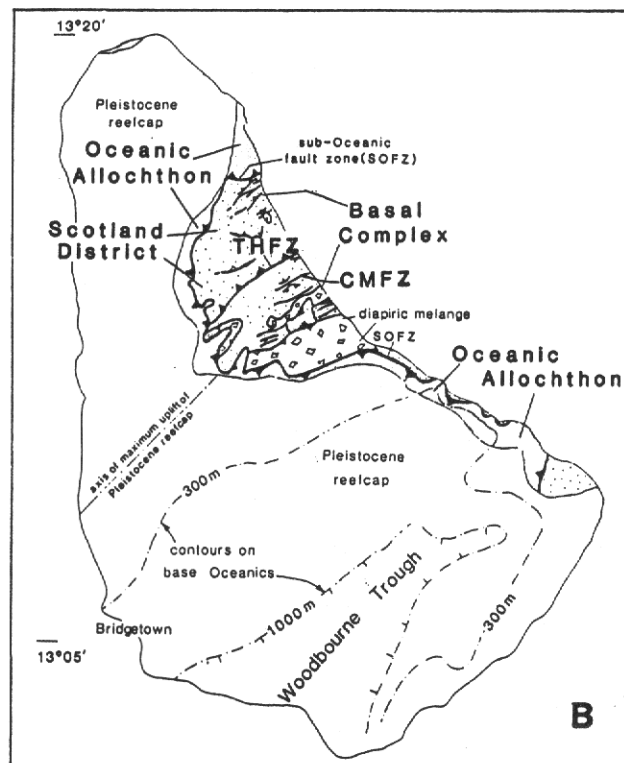
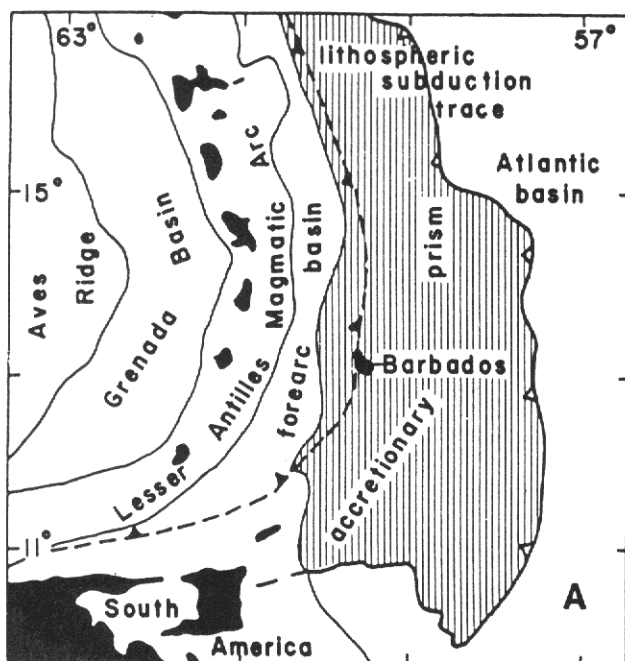


Figure 1. A) Index map showing location of Barbados Island at structural high of Lesser Antilles forearc; B) Major tectonostratigraphic units of the Scotland District of Barbados.

TYPES AND OCCURRENCES OF DIAGENETIC CARBONATE

Five different types of diagenetic carbonate have been identified among strata in the basal complex of Barbados: (1) calcite nodules, (2) calcite cement, (3) cone-in-cone calcite, (4) clay ironstone (Fe-bearing carbonate), and (5) dolomite cement. *Calcite nodules* occur within quartzose sandstones. The nodules are spherical to ellipsoidal and concentrated along certain stratal horizons or intervals. Sedimentary structures (convolute bedding, plane- and cross-lamination) are preserved within some of the nodules, and sedimentary lamination in adjacent sandstone typically deflects tangentially about the nodules. Continuous or blocky, pore-filling sparry *calcite cement* also occurs in quartzose sandstones, whose detrital framework and sedimentary structures are well preserved. *Cone-in-cone structures* occur in terrigenous mudstone as semicontinuous horizons of nested or interfering conical structures with lengths ≥ 3 cm, variable apical angles, and axes oriented orthogonal to bedding. Individual cones and cone segments are composed of fibrous calcite and are commonly separated by annular, cross-cutting seams of fine-grained noncalcareous particles, mainly clay minerals and quartz. *Clay ironstones* are gray to deep red, iron carbonate-cemented horizons in organic carbon-rich radiolarian mudstone and fine-grained, laminated sandstone. Diagenetic carbonate minerals in the ironstones include siderite and ferroan dolomite. The *Dolomite cement* with rhombohedral crystal morphology occurs in hemipelagic rocks.

RELATIVE AGE OF THE DIAGENETIC CARBONATE

All such diagenetic carbonate is interpreted as a product of early (predeformation) diagenesis from the

following lines of evidence. Firstly, sedimentary laminae deflect tangentially about the rims of large carbonate nodules, indicating precipitation of nodules prior to major compaction and porosity loss. Secondly, the carbonate has no apparent association with deformational structures such as folds, foliation, broken formation, or fault zones. Long axes of elliptical concretions and horizons of concretions and cone-in-cone carbonate are concordant to stratigraphic layering, even where such layering is folded. Thirdly, the orthogonal orientation of cone-in-cone axes with respect to host bedding is generally interpreted as a product of compaction during early diagenesis (Franks, 1969; Gilman and Metzger, 1967). Finally, at least some of the calcite-cemented sandstones and calcite nodules in sandstone have relatively high carbonate content (43-93 wt%; avg. ≈ 70 wt%). The values are higher than the maximum porosity of unconsolidated sand ($\sim 50\%$), suggesting displacement of sand grains during calcite crystal growth prior to major burial and compaction. Assuming that the diagenetic carbonate is a product of early diagenesis, its precipitation age probably is Eocene, the probable depositional age of strata in the basal complex of Barbados (Speed, 1988).

ISOTOPIC COMPOSITIONS AND INTERPRETATIONS

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions of the diagenetic carbonate range from -41.8 to $+24.2$ o/oo and -6.69 to $+5.24$ o/oo, respectively (Table 1; Fig. 2). Given an early diagenetic origin for the carbonate, the broad range of $\delta^{13}\text{C}$ values is most simply explained by a standard model of precipitation in various depth-related zones of organic burial diagenesis where $\delta^{13}\text{C}$ of dissolved CO_2 varies in response to differing modes of bacterial degradation of organic matter (Fig. 3;

Claypool and Kaplan, 1974; Gautier and Claypool, 1984). These zones are, from top down (Fig. 3): (1) the aerobic zone, (2) the sulfate reduction zone, (3) the zone of carbonate reduction (bacterial methanogenesis), and (4) the zone of thermal catalytic degradation and decarboxylation. Isotopic equilibration temperatures were calculated assuming equilibration with pore fluid compositionally equivalent to seawater of the nonglacial (Eocene) oceans ($\delta^{18}\text{O} = -1.2$ o/oo, SMOW; Shackleton and Kennett, 1975). The temperatures range from 9°-39°C. Organic diagenetic zones of carbonate precipitation can be interpreted based on carbon isotopic compositions and zonations, iron content, and differences in $\delta^{18}\text{O}$ composition and calculated equilibration temperature.

Isotopically heavy diagenetic carbonates (highly positive $\delta^{13}\text{C}$ values) probably precipitated in the zone of carbonate reduction (Fig. 3) where dissolved carbonate becomes ^{12}C -depleted due to preferential removal of light CO_2 to form biogenic methane (Claypool and Kaplan, 1974; Irwin et al., 1977).

The origins of isotopically light diagenetic carbonates are more difficult to interpret because each of the four zones of organic diagenesis may theoretically include ^{13}C -depleted CO_2 (Fig. 3). Although carbonate generally does not precipitate in the aerobic zone due to rapid loss of CO_2 , it may do so in rare cases and is iron-free due to the absence of reduced iron (Gautier, 1985). Carbonate precipitated in the sulfate reduction zone is also generally iron-free due to the preferred complexing of ferrous iron with reduced sulfur to form pyrite (Gautier and Claypool, 1984). Thus, iron-bearing ^{13}C -depleted diagenetic carbonate (clay ironstones, Fig. 3) probably precipitated in the zone of carbonate reduction rather than the aerobic or sulfate reduction zones. Rims and cross-cutting veins of iron-free calcite nodules (cannonballs, ellipsoids) are ^{13}C -depleted relative to their cores, suggesting precipitation during progressive burial at shallow depths in the aerobic and (or) sulfate reduction zones.

The organic diagenetic zones in which other samples of iron-free ^{13}C -depleted diagenetic carbonate originated are less certain but can be interpreted from $\delta^{18}\text{O}$ values and estimated relative precipitation depths. Samples with more negative $\delta^{13}\text{C}$ values (-29 to -40.2 o/oo) have positive $\delta^{18}\text{O}$ values (+0.14 to +0.58), suggesting precipitation at temperatures corresponding to relatively shallower depths near the boundary between the zones of sulfate and carbonate

reduction (Fig. 3). In contrast, samples with less negative $\delta^{13}\text{C}$ values (-7.8 to -14.5 o/oo) have negative $\delta^{18}\text{O}$ values (-2.75 to -6.53 o/oo), suggesting precipitation at temperatures corresponding to relatively greater depths within the zone of carbonate reduction (Fig. 3).

DEPTH OF PRECIPITATION

The oxygen equilibration temperatures of the early diagenetic carbonate can be used to calculate maximum precipitation depths. Assuming an Eocene bottom water temperature of 10°C (Savin et al., 1975) and a geothermal gradient on Barbados of 15°C/km (Larue et al., 1984), the calculated temperatures correspond to depths between 0 and 1,900 m below the seafloor.

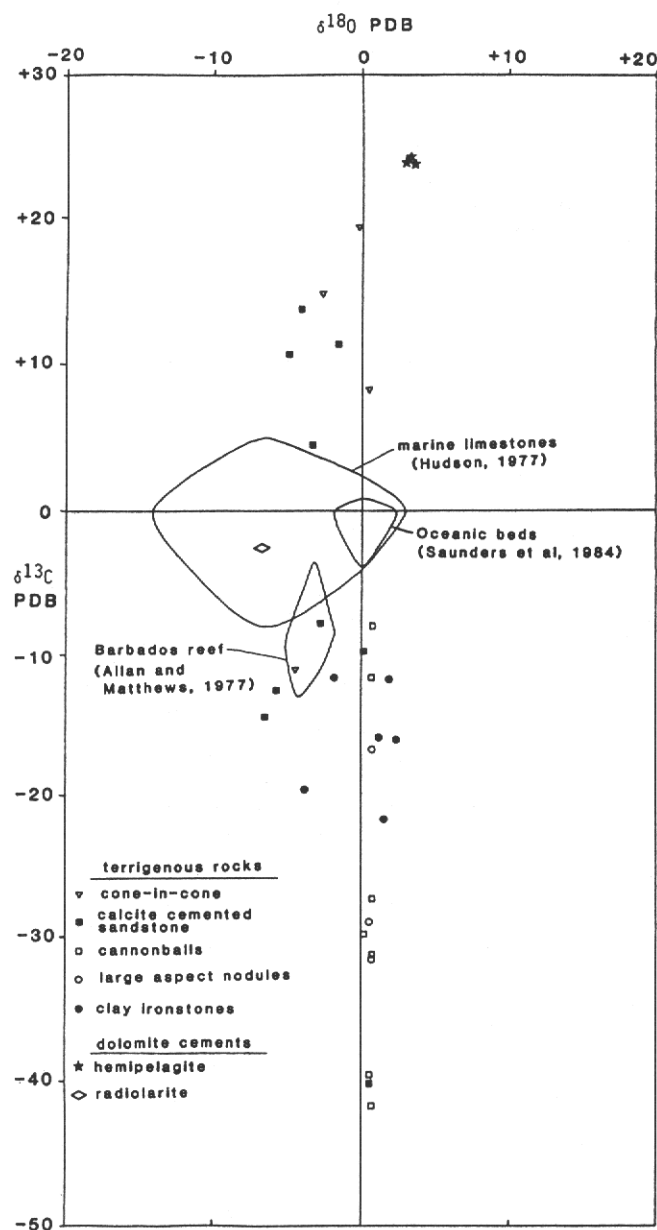


Figure 2. Stable carbon and oxygen isotopic compositions of early diagenetic carbonate in terrigenous and hemipelagic strata of Barbados. See text for discussion.

Table 1. Stable isotopic compositions of diagenetic carbonate

Type of Diagenetic Carbonate	$\delta^{13}\text{C}$ (o/oo)	$\delta^{18}\text{O}$ (o/oo)
cone-in-cone calcite in terrigenous mudstone	-11.1 to +19.4	-4.41 to +0.49
calcite concretions in quartz sandstone	-41.8 to -8.0	+0.05 to +0.79
clay ironstones	-21.8 to -11.7	-3.83 to +2.41
calcite cement in quartz sandstone	-40.2 to +13.7	-6.53 to +0.58
dolomite cement in hemipelagic strata	-2.5 to +24.2	-6.69 to +2.97

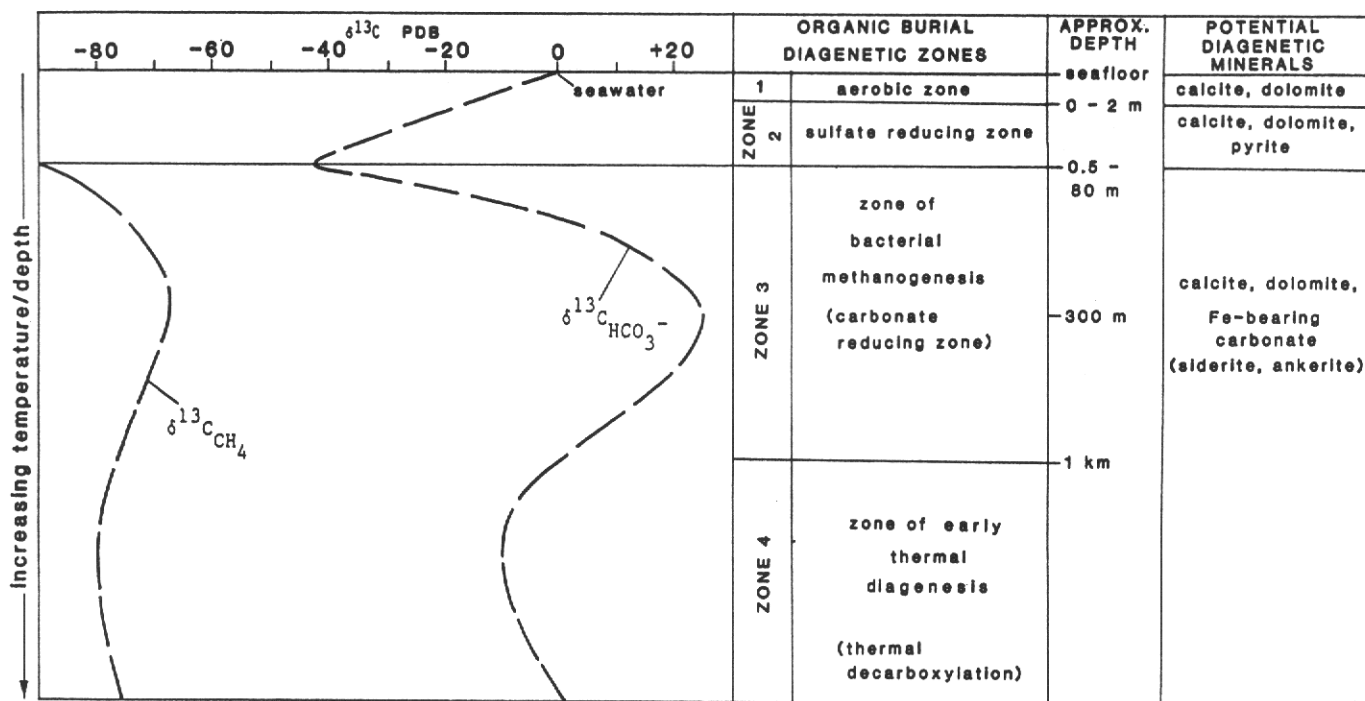


Figure 3. Generalized diagram showing succession of depth and temperature related zones of organic diagenesis and associated $\delta^{13}\text{C}$ compositions of CH_4 and HCO_3^- available for precipitation of diagenetic carbonate.

Carbonates formed in the aerobic and (or) sulfate reduction zones precipitated at depths ≤ 500 m and probably ≤ 100 m, based on the following reasoning. Firstly, outcrop evidence and high carbonate content indicate precipitation of such calcite nodules prior to major compaction and porosity loss. Secondly, the observed depth to the base of the sulfate reduction zone at DSDP sites of rapid terrigenous sediment deposition is generally ≤ 100 m. Finally, the $\delta^{18}\text{O}$ compositions of samples interpreted to have formed at shallow depths in the aerobic and (or) sulfate reduction zones (+0.05 to +0.79 o/oo) yield equilibration temperatures (9° - 12°C) like those of Eocene bottom water in the Atlantic Ocean (Savin et al., 1975). Regardless of the reality of such temperatures, the oxygen isotopic compositions are like those of benthic foraminifera in Eocene-Oligocene Oceanic beds (-0.03 to +2.30 o/oo; Saunders et al., 1984), indicating precipitation at or near the sediment/water interface.

The oxygen isotopic compositions of carbonates precipitated in the zone of carbonate reduction yield equilibration temperatures of 10° - 39°C . The temperature range and variable carbonate content of such samples suggest precipitation over a range of depths. Some have high carbonate content and $\delta^{18}\text{O}$ values like those of carbonate of the suprajacent sulfate reduction zone, suggesting precipitation near the top of the carbonate reduction zone at shallow depths (≤ 100 m) prior to major compaction and porosity loss. Others have low carbonate content and more negative $\delta^{18}\text{O}$ values, suggesting precipitation deeper within the carbonate reduction zone, at depths ≥ 500 m.

CONCLUSIONS

Diagenetic carbonate in terrigenous and hemipelagic rocks of the basal complex without apparent association with deformational structures is a product of early diagenesis. Isotopic compositions of such carbonate can be successfully interpreted using a standard model of organic burial diagenesis. The early diagenesis probably occurred in early-late Eocene time, prior to offscrape and accretion of beds of the basal complex. Some of the diagenetic carbonate has positive $\delta^{18}\text{O}$ values and zoned $\delta^{13}\text{C}$ values indicative of precipitation at relatively low temperatures and shallow depths (0-100 m). Other carbonate has more negative $\delta^{18}\text{O}$ values and positive $\delta^{13}\text{C}$ values, suggestive of precipitation at relatively greater temperatures and depths (500-1,900 m). Lack of systematic correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the diagenetic carbonate suggests spatial and (or) temporal variability in depth of organic burial diagenetic zones in the predeformed succession of marine strata.

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